

Dry Sorbent Injection of Trona for SO_x Mitigation

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ABSTRACT

Boilers, furnaces, metals and ceramics manufacture, and similar processes produce waste off-gases containing acidic species that, if released uncontrolled, are harmful to human health and the environment. The acid gases of primary concern are oxides of sulfur (SO_x) and hydrogen halides (HX). Gas scrubbing with alkaline solutions and solids is employed to reduce emissions of these acid gases. Different scrubbing technologies have been practiced for decades but least expensive to implement and simplest to operate are usually “dry scrubbing” or dry sorbent injection (DSI) systems. In DSI systems a dry powdered alkaline material is injected into the hot gas stream to neutralize the acidic species, and the resulting solid salts and remaining excess alkaline material is collected by a downstream particulate capture device. These systems are capable of high levels of acid gas reduction. Various alkaline materials, both chemically processed and naturally occurring, have seen application in dry scrubbing. Dry hydrated lime, a calcium based alkaline sorbent, is in wide use in dry scrubbing, largely because of its moderate cost and availability. However, sodium based alkaline sorbents such as sodium bicarbonate, nacholite, and trona can provide particular advantages that make them a superior choice in certain applications. A mechanically refined trona in both a powder and granular form is being used throughout these industries for SO_x mitigation and recently at a few glass production plants with good success and having economic advantages over other sorbents.. This paper will discuss the application process, important variables to insure optimal sorbent usage, the chemistry of the operation and data collected under various conditions including glass production. This paper summarizes the advantages of DSI systems and of dry injection of sodium based alkaline sorbents in particular.

INTRODUCTION

Fossil and waste fuel fired boilers and incinerators, primary and secondary metallurgical production processes, petroleum refinery catalyst regeneration, foundry operations, brick kilns, and other furnaces associated with production of various mineral products are common industrial sources of SO_x and HX are combustion or other high-temperature processes involving materials containing sulfur and/or halides.

When materials being processed in oxidizing atmospheres contain sulfur, the off-gases contain sulfur dioxide (SO₂) and small quantities of sulfur trioxide (SO₃) arising from excess O₂ and

catalysis. The SO₂ is present as a gas and the SO₃, which hydrolyzes with moisture in the gas stream, is usually present as an aerosol (sulfuric acid mist). When the materials being processed contain halides, such as fluorine, chlorine, or bromine, the off-gases will contain HF, HCl, or HBr. As with SO₃ these gases will also hydrolyze with available moisture to form acid aerosols. SO₂ is a criteria pollutant that effects both public health and the natural environment, and as such it has both primary and secondary National Ambient Air Quality Standards (NAAQS). In addition, Title IV of the 1990 Clean Air Act Amendments mandates reductions in SO₂ emissions from electric utilities.

DISCUSSION

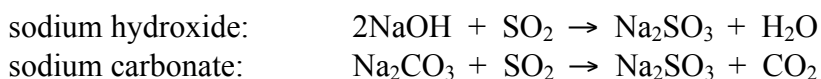
Although technologies exist for “cleaning” fuels or other materials before processing to remove acid gas precursors (sulfur and halides) and thereby limit acid gas emissions, pre-treatment is generally not economically viable. The release of acid gases to the environment is most often controlled by “scrubbing” the waste gases from the processes prior to release through a stack or other process vent.

Acid Gas Scrubbing Technologies

“Acid gas scrubbing technologies are usually based on multi-phase acid-base neutralization reactions. Neutralization reactions are typically fast and exothermic, and equilibrium conversions are high. However, in practice acid gas scrubbing neutralization reaction rates are mass-transfer limited and equilibrium conversions are not reached because the processes are continuous and available reaction times are limited. The effective rate of reaction and thereby the extent of acid neutralization realized in the available interfacial contact time (generally on the order of a few seconds in all types of scrubbers), depends largely on the rate of interfacial mass-transfer. The mass transfer rate, in turn depends largely on the physical and chemical form of the acid gases and the alkaline (basic) scrubbing reagents, and the physical characteristics of the systems used to bring them into contact with each other. The following sections outline the three most common approaches to alkaline scrubbing of acid gases.”¹

Wet Scrubbing

Wet scrubbing is an *absorption* process, in which the gas-phase is dissolved in a liquid a result of solubility. The dissolution rate is enhanced by using a mass-transfer device such as a packed-tower and a reactive scrubbing solution. The scrubbing solution is fortified to maintain the driving force for *absorption*. Both reactants are in solution as ionic species and only a small stoichiometric excess of material is needed to achieve high acid removal efficiencies. The rate-limiting step in wet scrubbing is the *absorption* of the acid gas into the liquid solution. The designs of mass transfer devices for this purpose focus on facilitating this *absorption* by counter-current gas/liquid flows, by maximizing interfacial area (between gas and liquid films), and by maintaining turbulent liquid and gas flow regimes. With the exception of large FGD (flue-gas desulfurization) systems on utility boilers, which employ limestone or hydrated lime slurries, the alkaline materials used in wet scrubbing are generally sodium based, since sodium salts are highly soluble in water. The most commonly used sodium based materials for wet scrubbing and their overall reactions with SO₂ are:



The gas exiting a wet scrubbing system is generally saturated with moisture from the scrubbing liquid. High inlet loadings of insoluble particulate matter can be problematic for such systems. Salts of acid gases removed by wet scrubbing systems are purged in scrubber blow-down and generally disposed as dissolved solids in wastewater. Depending on the process being controlled, this wastewater may also contain significant levels of insoluble, suspended solids.

Semi-dry Scrubbing

In semi-dry scrubbing the gas phase acid is also *absorbed* into a scrubbing liquid. However, rather than being a solution of alkaline material, it is typically a slurry prepared immediately prior to use. The reaction conditions are multi-phase and not as ideal as in a wet scrubber. A spray-dryer is typically employed as the contact device to avoid the problems of suspended solids in the liquid phase that occur in a packed tower. Interfacial area within the spray-dryer is maximized by mechanically atomizing the alkaline slurry into an open (usually vertical down-flowing) vessel in which gas flows are maintained in the turbulent regime, to facilitate mass transfer. Simultaneous heat and mass transfer from the hot gases to the slurry liquid transforms the aerosol particles of slurry into solid particles of acid salts and excess alkaline material that are collected downstream by a particulate capture device. Evaporation of the free water in the slurry results in quenching of the gases preferably at high temperatures. Salts of acid gases removed by semi-dry scrubbing systems are purged as solids with other captured particulate matter via an ESP or baghouse.

Dry Scrubbing

Acid gas removal by dry scrubbing also requires multi-phase mass transfer, but it occurs between the gas phase and the solid phase, rather than between the gas phase and the liquid and solid phases, as with wet and semi-dry scrubbing. The acid gas must first contact the solid surface of the dry alkaline material rather than being *absorbed* (dissolved) in a scrubbing liquid or slurry. Once the acid gas contacts the alkaline surface it is neutralized to form a solid salt that can remain as part of the solid particle alkaline material or “popped off” as a result of gas evolution. Chemically, these are less ideal neutralization reaction conditions than in wet or semi-dry scrubbers, since one reactant is in the gas phase and the other is in the solid phase. As a result, dry scrubbers usually require the greatest stoichiometric excess of alkaline material to achieve high acid removal efficiencies.

The dry sorbent injection (DSI) contact device can be simply the gas duct between the source and the downstream particulate capture device or a mixing chamber designed specifically to achieve contact time and mixing of the reactants. The key system performance factors are turbulent mixing of alkaline powder with hot gas while maximizing the time that the alkaline powder is suspended in the presence of the hot acid gases. There are systems in operation where DSI has been employed in conjunction with both a hot side and/or cold side ESP for particulate capture. Most studies have been done utilizing a fabric filter but commercially more sodium DSI systems are with ESP's. With an ESP the available acid-base contact time is limited to the time the alkaline powder and gas are in contact between the point of injection and the fields of the ESP. In a dry sorbent and semi-dry injection/fabric filter unconverted alkaline material in the suspended particulate matter becomes part of the filter cake on the bag filters and provides additional acid-base contact time as the cake accumulates on the bags between cleaning cycles.

In some cases the sorbent can decrease the resistance of the filter cake improving the APC operation.

Unlike wet and semi-dry scrubbing, evaporation of free water in scrubbing liquor and quenching of gases is not inherent in the dry scrubbing process. Sorbent injection temperatures are a function of the process, sorbent and APC device.

Dry furnace injection (DFI) where the dry alkaline material is injected directly into the process furnace at high temperature has been tried in many industries. The advantages of furnace injection are greater overall reaction time and higher reaction temperatures, producing faster reaction rates though this can upset the chemistry of the boiler creating other process concerns. Also, in certain the acid gases are generated by other APC devices. One such occurrence is SO₃ by the oxidation of SO₂ during NO_x abatement.

Technology Comparison

“Each of the technologies described in the previous sections is capable of removing high percentages of both SO_x. “Hence, the choice of which technology to apply is usually driven by a combination of cost and ease of operation & maintenance. The primary operating objective is to maintain conformance with the applicable regulatory limits for acid gas release, while incurring the minimum annualized total cost. The annualized total cost comprises both capital and operating & maintenance (O&M) costs. The annualized capital cost is the repayment of principal and interest on the funds borrowed to purchase and construct the acid gas scrubbing system. The largest component of the annualized O&M cost is typically the cost of the alkaline reagent, but it also includes energy costs associated with fans and pumps, and the costs of treatment and disposal of liquid and solid residues. The following Table 1 summarizes and qualitatively compares the various characteristics of the different acid gas scrubbing technologies.

Table 1 – Acid Gas Scrubbing Technology Comparison									
TECHNOLOGY		CHARACTERISTICS							
		Capital Cost to Install	Efficiency (reagent utilization)	Neutralizing Reagent Cost	Energy Cost	Process/Maintenance Complexity	Ease of Retrofit	Waste Water	Visible Plume
Wet Scrubbing	Calcium-based	HIGH	MEDIUM	LOW	HIGH	HIGH	LOW	YES	YES
	Sodium-based	HIGH	HIGH	HIGH	HIGH	HIGH	LOW	YES	YES
Semi-Dry Scrubbing	Calcium-based	HIGH	MEDIUM	MEDIUM	HIGH	HIGH	LOW	NO	NO
Dry Scrubbing	Calcium-based	LOW-MED	LOW-MED	MEDIUM	LOW	MEDIUM	MEDIUM	NO	NO
	Sodium-based	LOW	LOW-MED	MED-HIGH	LOW	LOW	HIGH	NO	NO

These advantages and disadvantages and their associated economics, form the basis for selection of an acid gas scrubbing system. Each type of system is best suited to a particular set of process and economic circumstances. The following paragraphs describe the dry injection technology in

greater detail and outline the circumstances under which it is likely to be the best process technology choice.”²

Dry Scrubbing

When compared with wet scrubbing or semi-dry scrubbing, the primary disadvantage of dry scrubbing or dry sorbent injection is poor sorbent utilization. Wet scrubbing and spray drying mixes the acidic and basic species together to form a solution or slurry. The main factor that limits conversion and necessitates a slight stoichiometric excess of alkaline reagent, is the need for the continuous phase contactor (eg. packed column) is to provide a driving force for the reaction. A greater stoichiometric excess of alkalinity is required for a semidry scrubber than with a wet scrubber. Dry scrubbing has to contend with particle size disparity, the inherent disadvantages of heterogeneous gas-solid resistance, interference of both the reaction products (shrinking core theory) and the unreacted alkaline material thus resulting in the greatest requirement for stoichiometric excess of sorbent.

Despite these disadvantages DSI systems are extremely simple to install and operate and are very cost effective compared with the more capital intensive wet systems. The only rotating equipment required is a small blower for dilute phase pneumatic conveying of the dry alkaline sorbent to the process gas ducting and possibly a mill. “The following are examples of circumstances in which a dry scrubber is better suited to an application than either a wet scrubber or a semi-dry scrubber:

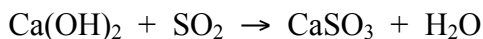
- ◆ The annualized cost of a dry injection system is lowest, or close enough to the other options to be influenced by factors to which costs cannot easily be assigned.
- ◆ The process throughput is not large enough to make semi-dry scrubbing economical (gas flows are less than approximately 100,000 acfm).
- ◆ Wastewater discharges from a wet scrubber cannot be permitted or are uneconomical to treat.
- ◆ Local electric power rates are high, making the higher system pressure drops associated with wet and semi-dry scrubbers too costly to operate.
- ◆ Moisture saturated exhaust gas or a visible steam plume from the stack are unacceptable.
- ◆ The process operation and maintenance complexity of wet and semi-dry scrubbers are incompatible with the facility operator’s organization.
- ◆ Handling hazardous chemicals such as sodium hydroxide, calcium oxide, and calcium hydroxide are not acceptable.
- ◆ Particulate capture equipment (eg. ESP or fabric filter) is already in operation and acid gas controls need to be retrofitted.”³

The remaining cost factor is the sorbent choice. That is:

1. The delivered cost of the sorbent per unit equivalent pollutant weight unit removed
2. The cost of spent sorbent disposal per unit pollutant removed.

Dry Injection Chemistry

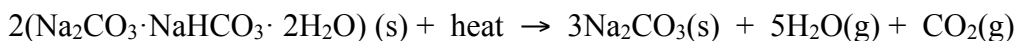
Dry injection (DI) systems can employ either calcium or sodium alkaline materials for neutralizing acid gases. With a calcium based system, dry hydrated lime (purchased and stored as Ca(OH)₂) is directly injected and the overall neutralization reactions are essentially the same as those for the semi-dry scrubber:



Sodium sorbent based systems the neutralization reactions are via sodium carbonate:



The source of the carbonate can be synthetic sodium bicarbonate, naturally occurring sodium bicarbonate (nacholite), or naturally occurring sodium sesquicarbonate (trona). When these materials are injected into a hot (oxidizing) gas stream they “calcine” according to:



“The theoretical stoichiometry and mass requirements for the different alkaline materials and reactions are summarized in Table 2.”⁴

Table 2 – Theoretical Chemical Comparison of Dry Alkaline Sorbent Materials							
Common Name	Chemical Name	MW	Neutralization Reactions	Theoretical Requirement		Purity	Practical Limit lb base lb acid
				Moles base Mole acid	lbs base lb acid		
Baking soda	Sodium bicarbonate	84.01	$2\text{NaHCO}_3 + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + 2\text{CO}_2$	2	2.62	99%	2.65
			$\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$	1	2.30		2.33
Hydrated lime	Calcium hydroxide	74.09	$\text{Ca(OH)}_2 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{H}_2\text{O}$	1	1.16	98%	1.18
			$\text{Ca(OH)}_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$	½	1.02		1.04
Nacholite	Sodium bicarbonate	84.01	$2\text{NaHCO}_3 + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + 2\text{CO}_2$	2	2.62	97%	2.70
			$\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$	1	2.30		2.37
Soda ash	Sodium carbonate	105.99	$\text{Na}_2\text{CO}_3 + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + \text{CO}_2$	1	1.65	97%	1.71
			$\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$	½	1.45		1.50
Trona	Sodium sesqui-Carbonate	226.03	$2(\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}) + 3\text{SO}_2 \rightarrow 3\text{Na}_2\text{SO}_3 + 5\text{H}_2\text{O} + 4\text{CO}_2$	2/3	2.35	97.5%	2.41
			$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O} + 3\text{HCl} \rightarrow 3\text{NaCl} + 4\text{H}_2\text{O} + 2\text{CO}_2$	1/3	2.01		2.12

Only the reactions between SO₂ and HCl and the alkaline material are shown in Table 2 for comparison purposes, but the stoichiometry for SO₃/H₂SO₄ and other HX is essentially the same.

Although it is not used directly as a DI alkaline material, for reasons explained later, soda ash is also included for comparison. As can be seen from this table, calcium sorbents have an theoretical stoichiometric advantage relative to sodium sorbents, due to the divalent cation (Ca^{++}), as compared with the monovalent cation (Na^+). Even with differing molecular weights factored in, the approximate 2 to 1 advantage translates roughly into mass so that the theoretical mass requirement for the sodium sorbents is roughly twice the theoretical calcium sorbent requirement. However, the theoretical requirements do not account for differing reactivities and assume that equilibrium conversions are reached. The different alkaline materials used in dry injection exhibit different reactivities and due to the nature of the processes, equilibrium conversions are never reached. A common measure of actual alkaline sorbent usage as compared with the theoretical requirement is the normalized stoichiometric ratio or NSR, defined as:

$$\text{normalized stoichiometric ratio} = \frac{\text{moles alkaline material actually injected}}{\text{moles alkaline material theoretically required}}$$

The well established axiom that combustion reactions are favored by “time, temperature, and turbulence” can also be applied to dry acid gas scrubbing. The process factors that have the most effect on alkaline reactivity and conversion are:

- ◆ available interfacial surface area,
- ◆ reaction temperature, and
- ◆ reaction time
- ◆ Turbulence/mixing

Surface Area

In dry scrubbers available area is determined by how much powdered alkaline material is suspended in the hot gas, by the individual alkaline material particle size, and by the average available surface area of each particle. Up to the point where solid particles of alkaline material drop out of the gas stream due to insufficient velocity to keep them suspended, the amount of alkaline material in the gas is driven by inlet acid gas loading. Individual particle size for “sorbent grade” alkaline materials is generally minimized by mechanical refinement to a practical mean diameter of 20 to 30 microns. In dust injection of sorbent being milled on site can improve utilization by lowering the particle size below this number. Another factor that has a great potential to effect available surface area for reaction is the interstitial pore area of the particles. Sodium sorbents such as sodium bicarbonate and trona are porous and their internal surface area can be several orders of magnitude greater than the outer surface area of the particle.

Although this characteristic is of limited importance with hydrated lime, it is significant with sodium sorbents. The reactions shown in Equations 12 and 13 above result in the explosive evolution of $\text{H}_2\text{O}(\text{g})$ and $\text{CO}_2(\text{g})$ from the source carbonate molecules, causing the solid particles to “pop-corn”, greatly increasing the available surface area of sodium carbonate within the

particles of alkaline sorbent material. Sodium carbonate (soda ash) itself is rarely used in dry scrubbing because this calcining does not occur and the surface area available for neutralization reaction, even with finely milled powder, is much less than in the “pop-corned” particles formed by calcining sodium bicarbonate/sesquicarbonate in the hot process gases.

Reaction Temperature

Although acid-base neutralization reactions are exothermic and the theoretical reactant conversion is negatively effected by temperature, as a practical matter the positive exponential temperature dependence of the reaction rate factor is far more important relative to conversion of alkaline material. Up to a point, the higher the gas temperature the faster the neutralization reaction and the greater the conversion of alkaline material to acid salts in the available reaction time. Dry injection systems often operate in the range of 250°F to 1500°F. Trials at many different process show that injection of trona 675°F can significantly increases the reactivity and conversion of the alkaline material, greatly reducing the effective NSR.

Reaction Time

“One of the aspects of dry scrubbing that can significantly offset the inherent limitation on reactant conversion is reaction time. In wet scrubbers the available reaction time is the time that the gas stream and scrubbing liquor are actually in contact. This time is generally on the order of a few seconds. In SD and DI systems that use ESPs for particulate collection, the situation is analogous. The available reaction time is the time that the gas stream and alkaline material are in contact - the time between injection of the alkaline material into the hot gas and the ESP fields removing the suspended particulate material.

In DSI/FF (and SD/FF) systems the neutralization reaction is a 2-phase process. Much of the conversion of alkaline material to acid salts occurs while the alkaline material is suspended in the gas but significant additional conversion can occur in the baghouse filter cakes between filter bag cleaning cycles. The typical contact time between reactants while the sorbent material is suspended in the gas stream is on the order of a few seconds. Exposure of alkaline material in the filter cakes to acid gas can range from several minutes to hours, depending on the baghouse cleaning cycle and the actual system pressure drop due to inlet dust loading. This additional residence time can increase the alkaline material conversion from a “once through” value of 30 to 50 percent, up to between 60 and 80 percent.

In calcium-based DI systems, the alkaline particle surface area does not benefit from the “pop-corn” effect of sodium materials. As a means of increasing sorbent utilization, calcium based DI processes often include systems for recycling collected particulate matter containing unreacted calcium in order to increase the conversion of alkaline material. Baghouse bottoms are collected and reinjected into the hot gas stream, increasing the total alkaline residence time and thereby the overall alkaline utilization. Depending on the system, single-pass conversions can range from 30 to 60 percent. Systems equipped with recycle can exceed 70 percent conversion of calcium. The disadvantage of sorbent recycle is that the dust loading in the hot gas going into the particulate capture device is significantly higher. With existing ESPs this may not be feasible and the particulate capture performance of existing baghouses may be significantly degraded. New baghouses designed for that dust loading will be much larger than they would be with the once-through dust loading and the greater the inlet dust loading the more frequently the bags will be cleaned. With sodium-based DI systems, the higher particle surface area available enables more

of the alkaline reactant conversion to occur while the material is initially suspended in the hot gas stream and allows greater conversion in the filter cakes on the bags in the baghouse. Hence, sodium-based systems are able to achieve high alkaline conversions without recycling baghouse bottoms to the hot gas stream, reducing the inlet loading of particulate matter that includes a significant fraction of material that is essentially inert, and thereby the required sizing of the particulate capture device”⁵.

Turbulence

The effect of mixing/turbulence has become increasingly important to achieve high utilization efficiencies of sorbents. It has been determined that the sorbent as well as the acid gases can channel or profile as the acids and sorbent travel down the duct to the particle control device. Mixing devices down stream from the injection point prior to the particulate collection device is important to improve the utilization efficiency of the trona especially when mitigating SO_x. Computer modeling should be considered to obtain the most cost effective DSI system.

Trona as a Sorbent for DSI

Recently several coal fired power plants have begun using dry sorbent injection of T200 a mechanically refined trona product. Dry sorbent injection is preferable to liquid injections due to the ease of handling, reduced risk of fouling downstream duct or equipment, and improved safety (including lower conveying pressures). Since T200 is a sodium compound it conditions the ash to lower its resistivity having a positive effect on the operation of both cold and hot side ESP's. Test results using the controlled condensation method verified visual indications that stack SO₃ levels below 10 ppm were routinely attainable without opacity excursions.

“Trona is a sodium based sorbent that is relatively low in cost, is highly reactive, and requires minimal capital for injection into the duct. Trona is typically injected in flue gas streams in various processes for acid gas mitigation. The use of trona for SO_x mitigation is well established. The use of sodium conditioning as an alternative to SO₃ conditioning has been documented.”⁶ The practical application of dry sodium injection for simultaneous SO₃ mitigation and ash conditioning is the subject of this report.

Background of Trona Ore

Trona's formation at Green River, Wyoming is the result of rapidly repeated evaporation cycles of Lake Gosiute approximately 50-60 million years ago. The original lake was fresh water and supported abundant flora and fauna. When the climate changed from humid to arid, Lake Gosiute evaporated and trapped the remnants of the once abundant life. The lake bottom became a mixture of mud and organic sediments that formed oil shale. Runoff water from the nearby mountains continued to supply sodium, alkaline earth, and bicarbonate to the lake. Since the rate of evaporation was high, the clear waters changed to brine that finally precipitated a sodium carbonate-bicarbonate compound known as the mineral “trona” (chemical formula: Na₂CO₃ • NaHCO₃ • 2H₂O). Alternating climates prevailed for about two million years. Periods of rains washed mud into the lake to cover previously formed carbonate type precipitates while interim

periods of arid climate produced new precipitates. This caused numerous beds of trona to be formed. In total, they contain billions of tons of trona and related minerals.

The tropical rains eventually returned to expand Lake Gosiute. This washed sand and mud from the surrounding mountains into its waters. Sediments of clay and shale built new formations as the geological evolution of the Green River Basin progressed. Buried under these sediments remain the trona beds that have become the basis of the present soda ash and sodium-based industry located around Green River, Wyoming.

Solvay Chemicals, Inc. currently mines trona ore from bed number 17 located at an approximate depth of 1500 feet. This ore body under Solvay's lease holdings is approximately 12 feet thick and of very high quality. Bed 17 will provide ore for many years; however, should the need arise, additional trona ore may be extracted from other beds as well.

Solvay Chemicals employs the "room and pillar" method of mining. Long drifts (tunnels) are mined with cross cuts at specified distances and the remaining pillars support the roof of the mine.

Solvay currently uses boring type miners and long wall mining to extract the ore. Roof bolting machines insert steel rods into the roof of the mined areas. This supports the immediate rock roof and prevents rock falls. Once cut, the ore is transported via shuttle car to a series of belt conveyors which discharge into underground storage bins. From these storage bins, the ore is hoisted to the surface in 20-ton capacity skips.

Solvay offers mechanically refined sodium sesquicarbonate (natural trona) to the merchant market. Coarse product exclusively is marketed and sold to the animal feed market by an outside company. Alternative products, Solvay T-50 (250-300µms) and T-200 (23µms), are marketed directly by Solvay for acid gas and acid neutralization applications.

Trona product operations are located in the ore-crushing portion of the soda ash plant. Trona ore is crushed and screened before being sent through a fluid bed dryer. The dryer serves to remove free moisture from the product and to separate the coarse (T-50) from fine (T-200) product. Trona products are stored in bulk quantity awaiting rail and truckload out. A bagging operation exists for the packaging of T50 products into 50-pound bags and both T50 and T200 in 2000-pound bulk sacks.

De-acidification of Acid Gases with Trona

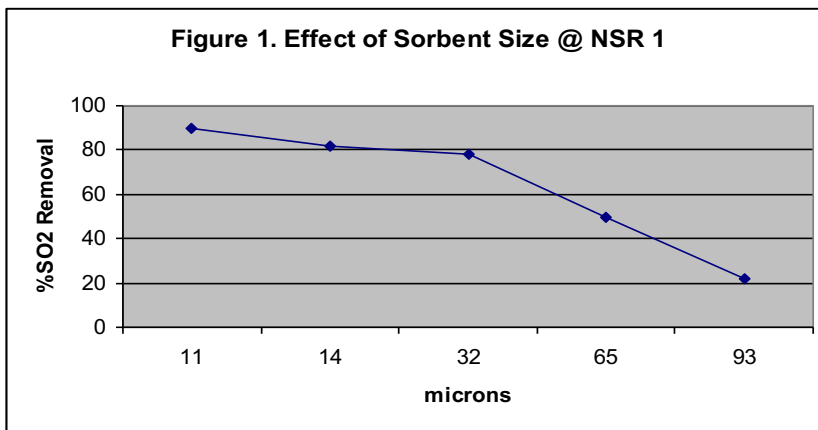
Trona is rapidly calcined to sodium carbonate when heated at or above 408°K (275°F). The "popcorn-like" decomposition creates a large and reactive surface by bringing un-reacted sodium carbonate to the particle surface for acid neutralization. The by-products of the reactions are sodium salts. For example the SO₂ chemistry is:

1. $2(\text{Na}_2\text{CO}_3 + \text{NaHCO}_3 + 2\text{H}_2\text{O}) + 3\text{SO}_2 \rightarrow 3\text{Na}_2\text{SO}_3 + 4\text{CO}_2 + 5\text{H}_2\text{O}$
2. $3\text{Na}_2\text{SO}_3 + 1.5\text{O}_2 \rightarrow 3\text{Na}_2\text{SO}_4$

Sodium carbonate is brought in contact with acid vapor in the flue gas stream by a simple direct injection of a sodium compound such as trona that will thermally decompose to form sodium carbonate. After the initial sorbent surface of the sodium carbonate has reacted with SO₂ to form

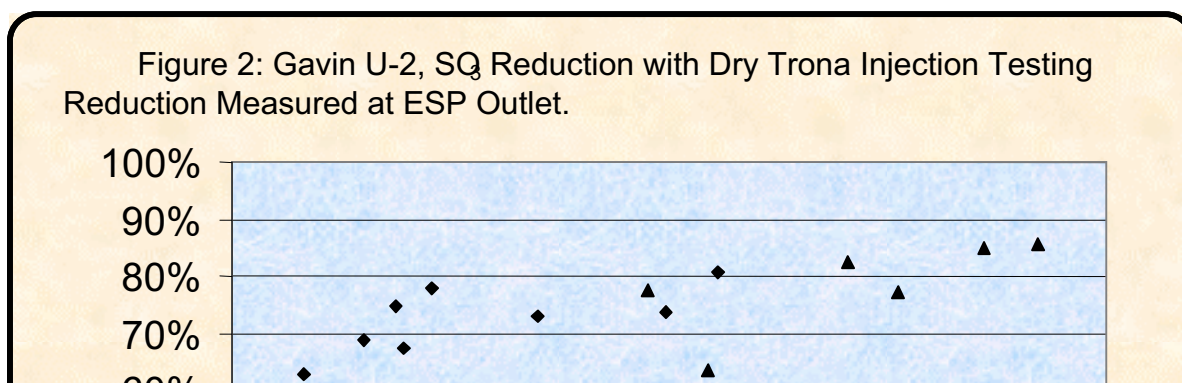
sodium sulfite, or sulfate, the reaction slows due to pore blockage -resisting gas phase diffusion of SO₂. In order for the reaction to continue, the sorbent particle must decompose further. This decomposition evolves H₂O and CO₂ gases into the surrounding atmosphere creating a network of void spaces throughout the particle. This process exposes fresh reactive sorbent and allows SO₂ once again to diffuse into the particle interior. This increase in surface area (‘popcorn effect’) is on the order or 5 to 20 times the original surface area.”

The particle size of the trona sorbent can have a dramatic effect on the removal efficiency of SO₂ as can be seen in Figure 1:

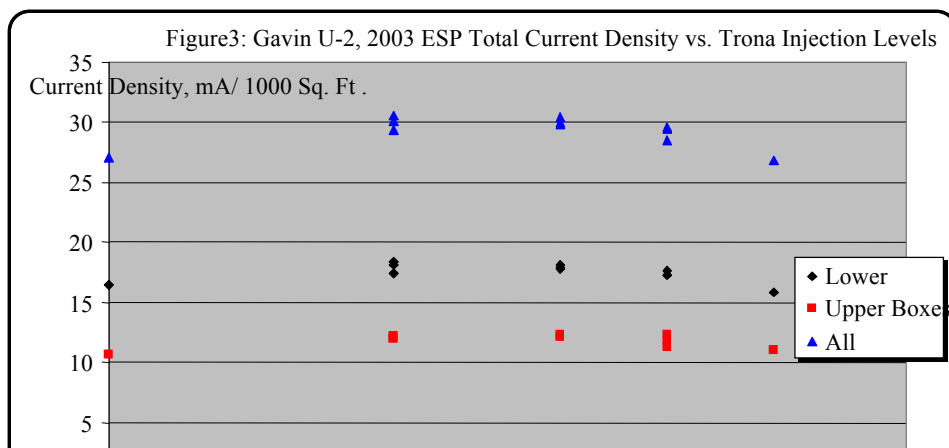


Cold Side ESP Conditioning⁷

“Referring to Figure 4, at a DSI rate of 2.9 TPH with the SCR O/S there is an indication that ESP conditioning may improve SO₃ removal efficiencies. The first data point was taken directly after trona injection began. There was no attempt to condition the ESP prior to this first test point. This resulted in a removal efficiency of about 63%. The removal was measured again at 2.9 TPH later in the test schedule. However, for the second data point at 2.9 TPH the ESP was well conditioned and a 78% removal was seen. Looking at these two data points in Figure 2 one can see that the unconditioned point is slightly above a 2.0 molar ratio (removing 63% SO₃) while the conditioned point is actually removing a higher percentage of SO₃ (78%) while being at a molar ratio slightly lower than 2.0.



Hydrated lime injection rates were limited to 2 to 2.5 TPH due to ESP performance degradation. No such degradation was noted with trona injection, see Figure 5. It did not appear that ESP performance was negatively impacted by trona injection. VI curves were also generated during trona injection with no indication of back corona. After a permanent system was installed, it was noticed that plant operators actually injected trona for the sole purpose of enhancing ESP performance. This was done when several T/R sets were O/S due to internal grounds. Hence, the trona system actually benefited ESP performance while SCRs were O/S.”⁶

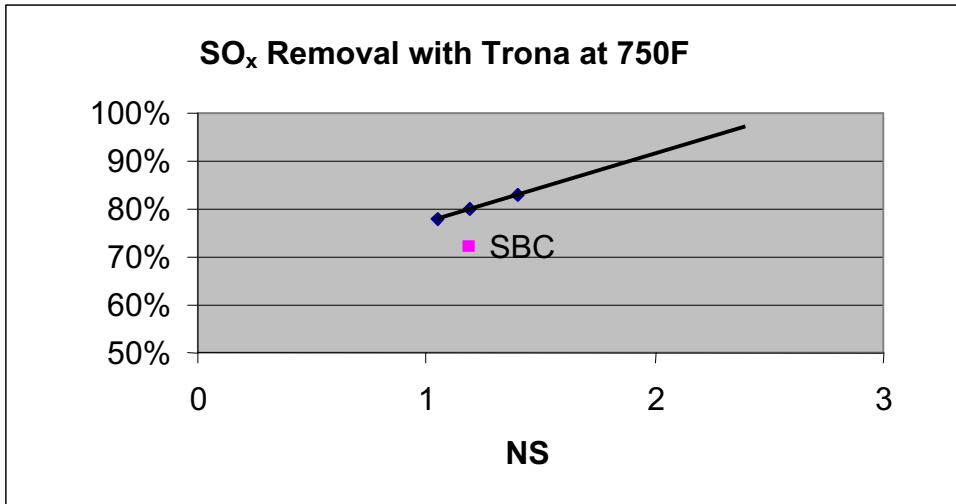


Hot Side ESP Experience⁷

Typically dry sorbent injection (DSI) has been done at temperatures lower than 400°F because of material of construction temperature limitations of the baghouse media and possible sintering of the sorbent crystal. What we have learned is that natural mechanically refined fine trona reactivity to sulfur oxides is improved as the injection temperature is raised unlike chemically refined milled sodium bicarbonate.

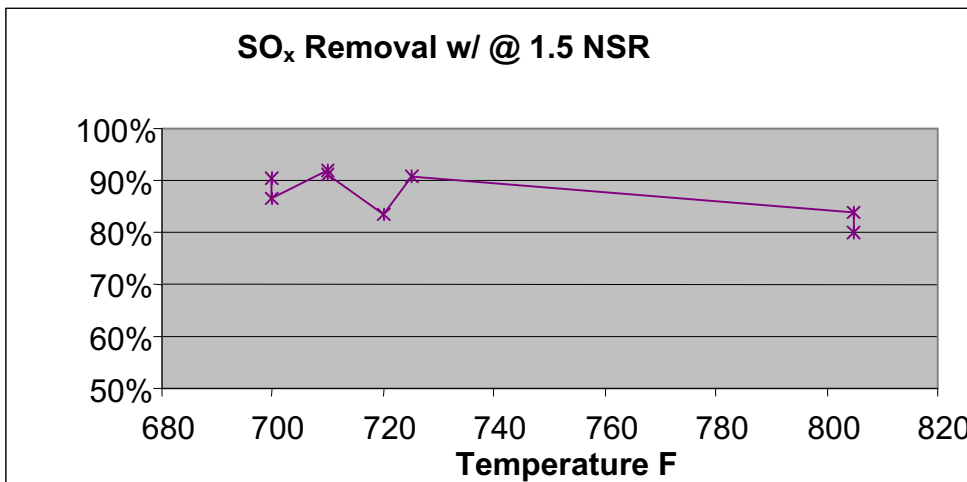
The graph below shows a study that varied the trona flow rate while holding all other process variables constant in comparison to sodium bicarbonate. This study was done in a commercial plant which used a hot side ESP (no baghouse) and SO_x concentrations of 800 ppm. Typically sodium bicarbonate will out perform mechanically refined trona. In this case trona removed 81% of the SO_x when milled sodium bicarbonate removed only 72% of the SO_x under the same situation. See Figure 6

Figure 4



The data shown in the graph below is from the same commercial process in which mechanically refined trona was injected into the flue gas stream at a 1.5 normalized stoichiometric ratio (NSR) rate while varying the injection temperature. Removals as high as 91% were achieved injecting T200 into a hot ESP w/o a baghouse. At this writing the T200 injection is being done at 725°F using 25% less trona than sodium bicarbonate and getting the same SO_x removal. SO_x removals as high as 91% have been demonstrated using trona at 725°F and at an NSR of 1.5. Please see below:

Figure 5



As can be seen in the graphs above high SO_x removals can be achieved at higher temperatures

than has been typically observed at lower temperatures unless a baghouse was used. Also, lower NSR values are needed for the high SO_x removal than observed in laboratory studies or actual plant operating data than milled sodium bicarbonate unless a baghouse was used.

Prior to injecting trona the “perf plates” of the hot side ESP would plug within days of injecting sodium bicarbonate but when using trona no pluggage was encountered and the system is operating trouble free for the last year.

CONCLUSIONS

In certain acid gas control applications, DSI is the simplest and least costly process to implement (new or retrofit), and the least costly to operate and maintain. Both calcium and sodium alkaline reagents are well proven in DSI applications. However, calcium hydroxide is a hazardous chemical with potential worker exposure hazards, whereas sodium bicarbonate/sesquicarbonate are considered to be nuisance dusts from the occupational exposure standpoint. The delivered cost of calcium and sodium reagents varies with location, but is more consistent with the chemically processed materials, dry hydrated lime and sodium bicarbonate, than with the naturally occurring materials nacholite and trona, which only have natural deposits in certain parts of the country. The sodium sorbents are generally more costly than the calcium sorbents, although the material cost (less freight) of dry hydrated lime and trona are similar. Among the sodium sorbents, nacholite and synthetic sodium bicarbonate are slightly more efficient for SO_x reduction, while trona is slightly more effective for HX reduction. The delivered cost of synthetic sodium bicarbonate is significantly higher than nacholite, and nacholite is generally higher than trona.

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7. *Ibid*

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